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H01L 21/285

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(71) Applicant: **ULVAC JAPAN LTD**

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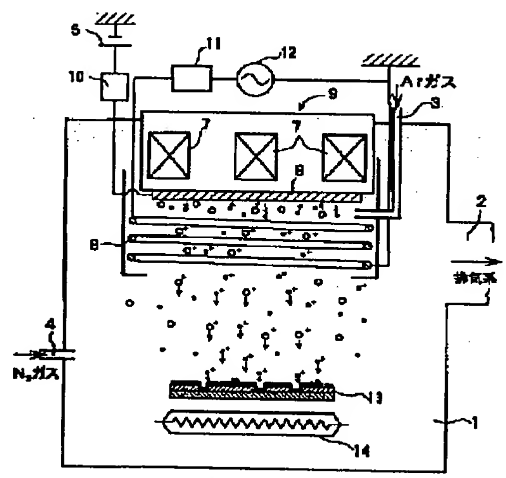
MORITA TADASHI
YAMAMOTO NAOSHI

(54) **METHOD FOR FORMING COMPOUND BARRIER FILM IN SILICON SEMICONDUCTOR**

(57) Abstract:

PROBLEM TO BE SOLVED: To provide the method for forming the compound barrier film free from steps in one process by a single device.

SOLUTION: A magnetron cathode 9 having a metal target 6 connected to a DC power source 5, a magnet 7 therebehind, and a RF coil 8 to improve the ionization rate forward of the target, is provided in a vacuum chamber 1 to control the power input to the target and the RF coil for generating the plasma, and the flow rate of the inert gas and the reactive gas to be introduced in the vacuum chamber, and a thick compound barrier film is formed by alternately repeating the formation of the metallic film on the surface of a silicon semiconductor substrate 13 provided opposite to the target and the compounding of the metallic film.



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Ｈ０１Ｌ	21/203		Ｈ０１Ｌ	21/203	S
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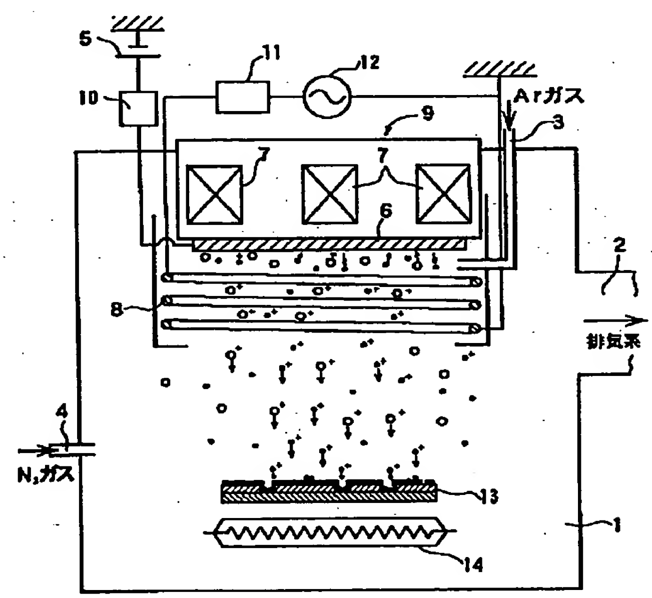
(54)【発明の名称】　シリコン半導体に於ける化合物バリア膜形成方法

(57)【要約】
【課題】段差切れのない化合物バリヤ膜を単一の装置により１プロセスで形成する方法を提供すること
【解決手段】真空室内１に、直流電源５に接続されたメタルターゲット６とその背後の磁石７及び該ターゲットの前方のイオン化率を高めるＲＦコイル８を備えたマグネトロンカソード９を設け、プラズマ発生のための該ターゲット及びＲＦコイルへの投入電力と、該真空室内へ導入するスパッタ用不活性ガス及び反応性ガスの流量とを制御し、該ターゲットに対向して設けたシリコン半導体基板１３の表面にメタル膜の成膜と該メタル膜の化合物化を交互に繰り返して厚い化合物バリア膜を形成する



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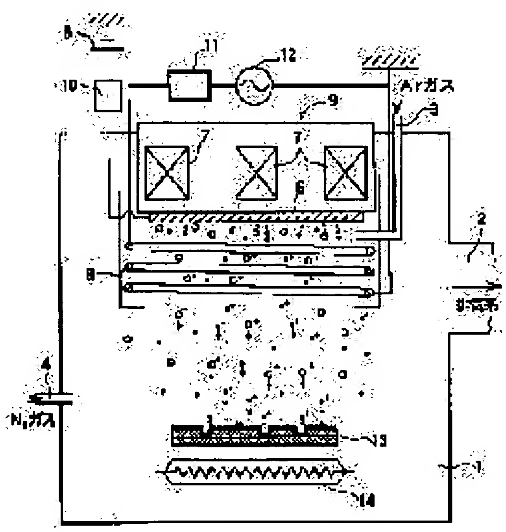
SOLUTION: A magnetron cathode 9 having a metal target 6 connected to a DC power source 5, a magnet 7 therebehind, and a RF coil 8 to improve the ionization rate forward of the target, is provided in a vacuum chamber 1 to control the power input to the target and the RF coil for generating the plasma, and the flow rate of the inert gas and the reactive gas to be introduced in the vacuum chamber, and a thick compound barrier film is formed by alternately repeating the formation of the metallic film on the surface of a silicon semiconductor substrate 13 provided opposite to the target and the compounding of the metallic film.



* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the method of forming the compound barrier film applied to the metal wiring process of a silicon semiconductor device etc.
[0002]
[Description of the Prior Art] Conventionally, in the metal wiring process of a silicon semiconductor device, forming compound barrier films, such as TiN, in the front face of a silicon semiconductor substrate for diffusion prevention as a ground of this in advance of formation of main wiring metal is performed. The formation method by the spatter using the planar magnetron cathode as the formation method of this compound barrier film and the formation method by CVD are learned. The method of forming a direct compound barrier film on a ground by the reactant spatter, when based on a spatter, A metal layer is made to deposit first by the simple spatter on a ground at a spatter room. subsequently, the method of making this metal layer react by this controlled atmosphere only by heating in reactant gas atmosphere, such as nitrogen gas, in a reaction chamber, and forming a compound barrier film -- or The method of forming a metal layer first by the simple spatter on a ground at a spatter room, and making this metal layer react by this controlled atmosphere in a reactant gas atmosphere subsequently excited with the plasma of a reaction chamber, and forming a compound barrier film is used. When based on CVD, the direct compound barrier film is formed on a ground.
[0003] Moreover, as a spatter cathode, while forming a magnet behind a target, the inductive-coupling RF plasma support magnetron cathode which prepared RF coil ahead of this target is proposed by the applicant (JP,6-41739,A). This cathode can maintain generating of plasma in a high vacuum, and has an advantage with little generating of an impurity or a secondary product.
[0004]
[Problem(s) to be Solved by the Invention] by the method by the above-mentioned reactant spatter, although the compound barrier film could be formed, when the level difference sections, such as a contact hole and a hole of a beer hall, be formed on the surface of the substrate, the so-called "level difference piece" with which the compound barrier film a of TiN as often showed in drawing 1 near the entrance of a hole be finely cover with the ground layer b of an insulator (SiO2) be generated, and there be a fault that barrier nature be tore from here. Compound barrier films, such as a silica by which this is used for a ground, and its compound, TiN, are considered for a compound barrier film to go out in the level difference section by which boundary tension is greatly pulled from the 2-way from which so-called "wetting" differs since it is bad.
[0005] On the other hand, by the method of carrying out thermal reaction of the above-mentioned metal layer, the compound barrier film with which the metal layer deposited on the ground by the spatter was formed in order that a silica, and its compound and "wetting" of a ground could cover a ground finely since it is good, and they might subsequently compound-ize this metal layer by thermal reaction covers a ground finely, and a level difference piece is not generated. However, by this method, for barrier film formation, the separate equipment which considers the processing as a spatter and two processes of

thermal reaction is required, and there is un-arranging [to which creation cost becomes high].
[0006] Moreover, although a compound barrier film without the same level difference piece as the thermal reaction method of the aforementioned metal layer can be formed by the method of carrying out the plasma reaction of the above-mentioned metal layer, there are the following two problems by this method. It is the problem that the separate equipment which considers the processing as a spatter and two processes of a plasma reaction is required for one of them, and creation cost becomes high, and since another has a limitation in the thickness of the compound barrier film which can be formed at a plasma reaction, as drawing 2 sees, it is the problem that the barrier nature becomes often inadequate. That is, it is the problem that remain for the surface portion of a metal layer to serve as a compound barrier film, and the whole metal layer does not become a compound barrier film. Although the controlled-atmosphere component by which plasma excitation was carried out advances into a layer by diffusion from the front face of a metal layer and a reaction advances at a plasma reaction, since it becomes inadequate [the low plasma reaction of temperature] from the aforementioned thermal reaction spreading reaction temperature into a metal layer, the reason out of which a limitation comes to the thickness of this barrier film is considered because a thick reaction layer cannot be formed.
[0007] Furthermore, having un-arranged [to which another isolated system is completely needed, and creation cost becomes high], since CVD serves as a completely different equipment configuration from a spatter, cannot take the adjustment of equipment with the main metal wiring process performed by the spatter after barrier film formation and cannot carry out [multi chamber]-izing, although a compound barrier film without a level difference piece can be formed in the above-mentioned CVD.
[0008] this invention aims at offering the method of forming a compound barrier film without a level difference piece in one process with single equipment.
[0009]
[Means for Solving the Problem] In this invention, the magnetron cathode equipped with RF coil which raises the ionization rate ahead of the metal target connected to DC power supply, its magnet in back, and this target is formed in a vacuum chamber. The injection power to this target and RF coil for plasma generating, The flow rate of the inert gas for spatters introduced into this vacuum chamber and reactant gas is controlled. The above-mentioned purpose was attained by repeating compound-ization of membrane formation of a metal film, and this metal film on the front face of a silicon semiconductor substrate which countered this target and was prepared by turns, and forming a thick compound barrier film in it. It is convenient to manufacture this RF coil with the metal of the same quality of the material as the above-mentioned metal target, and it is desirable to connect this metal target to DC power supply through an unusual electric discharge prevention circuit.
[0010]
[Embodiments of the Invention] When the gestalt of operation of this invention is explained based on a drawing, drawing 3 is the sputtering system used for operation of this invention, and the sign 1 of this drawing shows the vacuum chamber which formed the reactant gas inlet 4 which introduces the exhaust port 2 which stands in a row in a vacuum pump, the inlet 3 of the gas for spatters, such as argon gas, and the reactant gas of N2 grade. In this vacuum chamber 1, the magnetron cathode 9 equipped with the RF coil 8 which raises the ionization rate ahead of the metal targets 6, such as a product made from Ti, the magnet 7 in back of those, and this target 6 which were connected to DC power supply 5 through the unusual electric discharge prevention circuit 10 is formed. This cathode 9 is well-known as the above-mentioned inductive-coupling RF plasma support magnetron cathode, the RF coil 8 surrounds the circumference of the front of the metal target 6, and is prepared, and power is supplied to this from the RF power supply 12 through a matching box 11. For example, it is the substrate with a diameter of 2 inches for silicon semiconductor devices which countered with this target 6 and was prepared that 13 should form the compound barrier film for diffusion prevention, and the level difference sections, such as a contact hole, and a beer hall or a slot, are beforehand formed in the front face, and a metal wiring film is formed after formation of a compound barrier film. This RF coil 8 is formed in Ti of this metal target 6 and this quality of the material, and when required, it makes the interior circulate through cooling water. 14 is a heater for substrate heating.

[0011] In order to form a compound barrier film in a substrate 13 by the reactant spatter using the equipment of drawing 3 , after exhausting the inside of a vacuum chamber 1 first, carrying out proper quantity introduction of the argon gas for spatters from the inlet 3 near the cathode 9 and adjusting a pressure, a substrate 13 is heated at a heater 14 and substrate temperature is made into necessary membrane formation temperature. RF power is supplied to the metal target 6 at a direct current power and the RF coil 8, respectively. Plasma occurs ahead of a target 6 by this, the spatter of the target 6 is carried out by ion, and the metal particle by which the spatter was carried out deposits on a substrate 13. Injection power to a target 6 is made into zero in the place whose metal is about dozens ofA and which was deposited in the shape of a film very thinly, and where only the RF power to the RF coil 8 is switched on, reactant gas is introduced from the reactant gas inlet 4. Thereby, the spatter of the target 6 is hardly carried out, but the introduced reactant gas reacts promptly with the metal film deposited since it was excited-ion-ized with the plasma of the RF coil 8, and serves as a compound barrier film. Since this deposited metal film is very thin, it turns into a compound film which combined nearly completely to the interior of a thin film.
[0012] Then, the spatter process of said target 6 and the compound-ized process by introduction of reactant gas are repeated, and an about 100A ultra-thin compound barrier film is formed on a substrate 13. The compound barrier film obtained by this has good barrier nature, though it is ultra-thin. At a target 6, use of various kinds of metal which forms a compound barrier film is possible, for example, if Ta and W are used, the barrier film of TaN and WN can be formed and compound barrier films various by choosing the material and the reactant gas of a target suitably can be formed.
[0013] It depends for the ionization of a metal particle or reactant gas by which the spatter was carried out, or the grade of excitation on the RF power mainly supplied to the RF coil 8 depending on the direct current power which mainly supplies the rate of sedimentation of the metal to this substrate 13 to a target 6. The latter reason is considered for according to the same post ionization mechanism as the ion plating of being ionized when the neutral metal particle by which the spatter was carried out passes through the plasma zone which the RF coil 8 builds. Since it is mainly dependent on the collision frequency of an electron and a gas particle, generally the grade of this ionization and excitation has the large one where the pressure of gas is higher. However, in the so-called long slow spatter which the distance between a substrate and a target has detached about 3 to 8 times from the distance in conventional planar magnetron-sputtering equipment, since it will be quenched by the collision with a target and the inert gas between substrates if gas pressure is high even if it excites with the plasma in RF coil (cooled), the amount of ion which reaches a substrate as a result decreases. Therefore, in such arrangement, it becomes more remarkable as an amount of ion which reaches a substrate under the low pressure of 2x10 to 3 or less Torrs. In case this metal film is made to deposit, an ionization efficiency increases, it is precise with sufficient covering nature, and an about dozens of goodA crystalline very thin metal film may be made to deposit on the ground of a substrate 13 by supplying RF power not only to the direct current power to this target 6 but to the RF coil 8 simultaneously. and the plasma there is almost no metal by which a spatter will be carried out if reactant gas is introduced in the state where made the direct current power to a target 6 into zero, and it considered only as the RF power to the RF coil 8, and according to the RF coil 8 -- excited ion -- the pole which were-izing [the pole] and was deposited -- it reacts quickly with a thin metal film, and this film is used as a compound barrier film nearly completely
[0014] In addition, in a compound-ized process with the RF coil 8, since coating of a metal film is not performed by the spatter particle from a target 6 to the front face of the RF coil 8, although contamination that the spatter of the front face of the RF coil 8 which became unreserved is carried out by the inductively coupled plasma discharge, and the spatter particle of the coil strip adheres to the front face of a substrate 13 can be considered, such contamination can prevent the RF coil 8 by producing with a target 6 and this quality of the material.
[0015] Moreover, in the case of plasma excitation and ionization of this reactant gas, the front face of a target 6 also reacts, a compound layer is formed there, and the direct current discharge in the following spatter process may become unstable. If the small compound and small insulator of electrical

conductivity are formed in a target front face, in a direct current discharge, a positive charge is charged on the front face, it will be because the potential difference between a cathode (target) and an anode (substrate) is committed in the direction which disappears, and electric discharge will become unstable or this will bring a result which electric discharge stops. When it was made to generate right potential at a fixed rate and became this right potential as the unusual electric discharge prevention circuit 10 is made to be placed between DC power supplies 5 of this target 6 and it was shown in drawing 4 that what is necessary is just to neutralize the positive charge with which the target front face was covered by the electron from plasma therefore in order to have canceled this state, it was made to neutralize the positive charge with which drew the electron from plasma in the target front face, and the target front face was covered.

[0016]

[Example] Equipment equipped with the inductive-coupling RF plasma support magnetron cathode shown in drawing 3 was used, and about 100A very thin compound barrier film of TiN was formed on the substrate 13 of a silicon semiconductor device. The RF coil 8 is the product made from Ti which carried out water cooling, and connected DC power supply 5 to the target 6 made from Ti through the unusual electric discharge prevention circuit 10. Moreover, it enables it to introduce argon gas from an inlet 3 as spatter gas, and enabled it to introduce N2 gas from the reactant gas inlet 4 as reactant gas. The diameter of a cathode 6 is 2 inches. Distance between a substrate and a target was set to 200mm.

[0017] In advance of formation of this compound barrier film, 6x10-4Torr and target injection power were made DC50W regularity for the argon spatter gas pressure in a vacuum chamber 1, the injection power to the RF coil 8 was changed, and change of the ion current which flows into Ti film rate of sedimentation and the substrate to a substrate 13 top was measured. In addition, in order to enable it to measure the ion current (Ti+, Ar+) which flows into a substrate to a substrate 13, a direct current was impressed -50V. The result is like drawing 5 and it turns out that Ti film rate of sedimentation is seldom dependent on the injection power to the RF coil 8. Change of Ti film rate of sedimentation when changing a target direct current power to drawing 6 by making injection power to the RF coil 8 into a parameter was shown. Thereby, under these conditions, it is proportional to the power supplied to a target 6, it turns out that it is hardly influenced by the injection power to the RF coil 8, and Ti film rate of sedimentation is in agreement with the result of drawing 5 . on the other hand, the ion current which flows into a substrate 13 is increasing rapidly with the injection power to the RF coil 8, and this inductive-coupling RF plasma support magnetron-sputtering method is very effective in ionization promotion of a spatter particle -- it is ******(ing) The ion which flows into this substrate is Ti ion and Ar ion, and the result which investigated which ion is which grade is drawing 7 . This measurement attaches a quadrupole mass spectrometer with an energy analyzer in the position of a substrate 13, and when it carries out the spatter of the Ti target, it measures the energy distribution of the kind and amount of the ion which flows into a substrate. Here, injection power to the RF coil 8 is considered as 40W regularity, and the example to which the target injection direct current power was changed is shown. drawing 7 -- a direct current power -- stopping -- the injection power to RF coil -- relative -- increasing (DC power being reduced) -- it turns out that gas is mainly ionized and that the energy of ion shifts to a high-energy side Since it is thought that reactant excitation of a gas happens preferentially similarly when reactant gas, such as nitrogen, is added as a controlled atmosphere, this is conditions very convenient although a deposited metal film is made to react with reactant gas and a compound film is created. On the other hand, when a direct current power is enlarged relatively, it turns out that the ionization of a metal particle by which the spatter was carried out progresses, and a metal film precise and good under these conditions (reactant gas is not added) can be deposited.

[0018] Based on this result, the compound barrier film of TiN which was excellent in barrier nature with a necessary thickness of about 100A with the equipment of drawing 3 repeatedly according to the procedure which showed the spatter process which deposits Ti metal film, and the compound-ized process which compound-izes the film by plasma nitriding to drawing 8 was formed. Spatter argon gas pressure presupposed that the temperature of 8x10-4Torr and Si substrate is fixed 300 degrees C.

[0019] In detail, RF power to 80W and the RF coil 8 was set to 30W, 20sccm(s) and N2 gas were set to

0sccm for Ar gas, the spatter of the direct current power to a target 6 was carried out for 30 seconds on this condition, and the substrate was made to deposit Ti metal film with a thickness of about about 20A first. Then, 30W were maintained [the direct current power to a target] for the RF power to 0V and the RF coil 8 as they were, the flow rate of spatter argon gas was decreased to 5sccm(s), N2 gas was introduced into 20sccm vacuum chamber, the plasma nitriding of this Ti metal film that was generated for 60 seconds and deposited only the inductively coupled plasma with the RF coil 8 was carried out, and it considered as the TiN film. Furthermore, the following metal film was made to deposit on the spatter conditions of the aforementioned Ti metal film in the thickness of about 20A on this TiN film, and this following metal film was nitrided on the aforementioned compound-ized conditions and these conditions. Thus, the TiN film of about 100A of repeats was formed in the substrate for the spatter process and the compound-ized process 4 times.

[0020] And one example of the result which measured the distribution of the depth direction of the composition element of the TiN film created on Si wafer substrate on the same conditions as this by the Auger electron spectroscopy (AES) is shown in drawing 9 . It turns out that all the deposited films serve as TiN and it differs from the conventional film (drawing 2) which has nitrided only the front face greatly.

[0021] Although the example of TiN was shown here, it is applicable to membrane formation of various compound barrier films, such as TaN and WN. In addition, this invention is equipped with both the mechanism which carries out the spatter of the metal, and the mechanism which carries out plasma excitation of the controlled atmosphere in the same chamber, and if they can control almost independently, it can apply it theoretically. Therefore, it is not necessary to say that it can apply to the sputtering system which has installed RF coil in the middle of a target and a substrate, for example, an efficient consumer response sputtering system, etc. also except the equipment shown in drawing 3 . Moreover, although the silicon-substrate metal wiring process was described here, application in various electronic equipment device thin film production processes, such as a flat display and the thin film magnetic head, is possible. Furthermore, although the spatter process of metal deposition of a compound barrier film and the compound-ized process by the plasma reaction were repeated by turns here instead, even the 1st layer with bad ground and "wetting" or the following layer [2nd] may be created by this method, and a compound layer may be formed at once by the reactant spatter after it.

[0022]

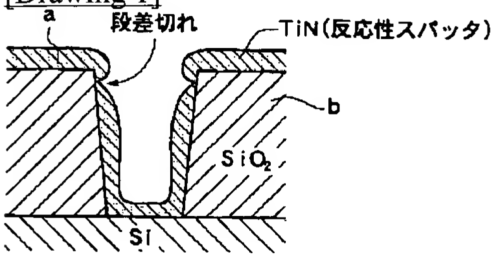
[Effect of the Invention] When based on this invention as mentioned above, the magnetron cathode equipped with RF coil which raises an ionization rate is formed. The injection power to a target and RF coil, since the flow rate of the inert gas for spatters introduced into this vacuum chamber and reactant gas is controlled, a substrate is resembled and it was made to repeat compound-ization of membrane formation of a metal film, and this metal film by turns A compound barrier film without a level difference piece can be formed in one process with single equipment, and there are effects, like membrane formation cost becomes cheap.

[Translation done.]

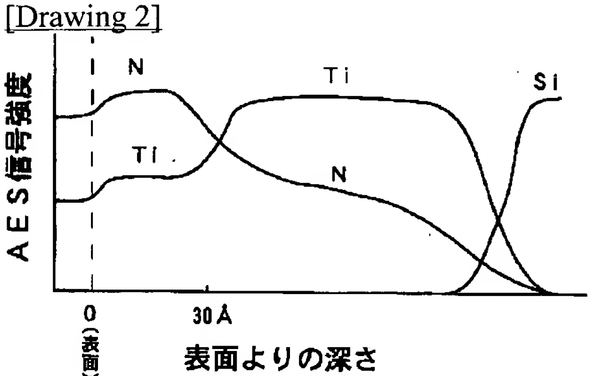
NOTICES *

DRAWINGS

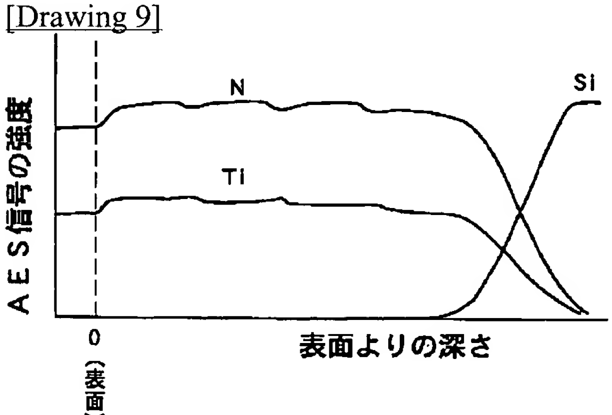
[Drawing 1]



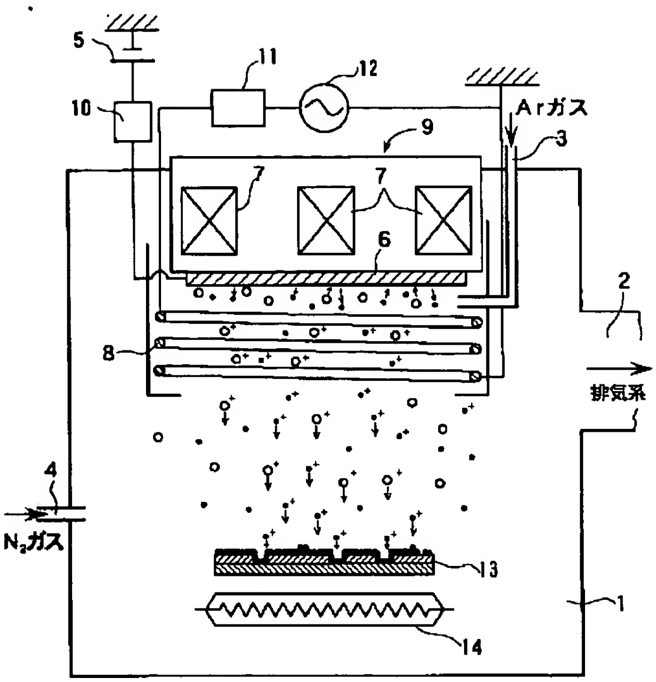
[Drawing 2]



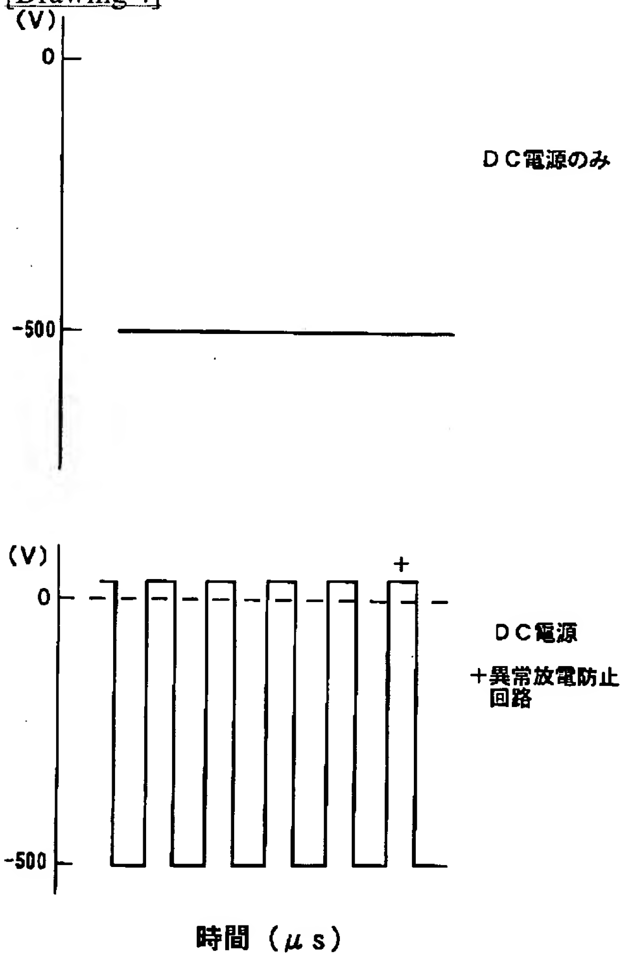
[Drawing 9]



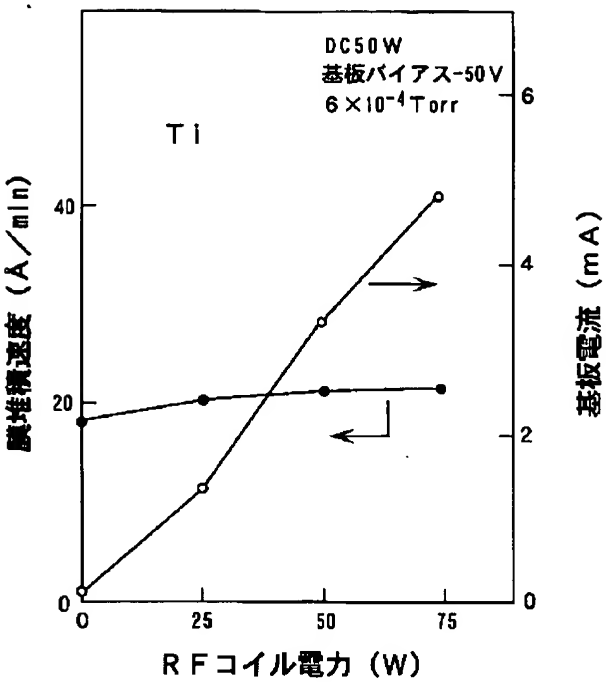
[Drawing 3]



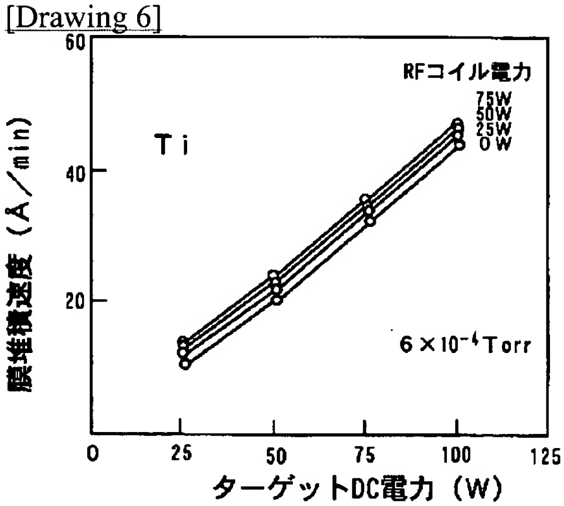
[Drawing 4]



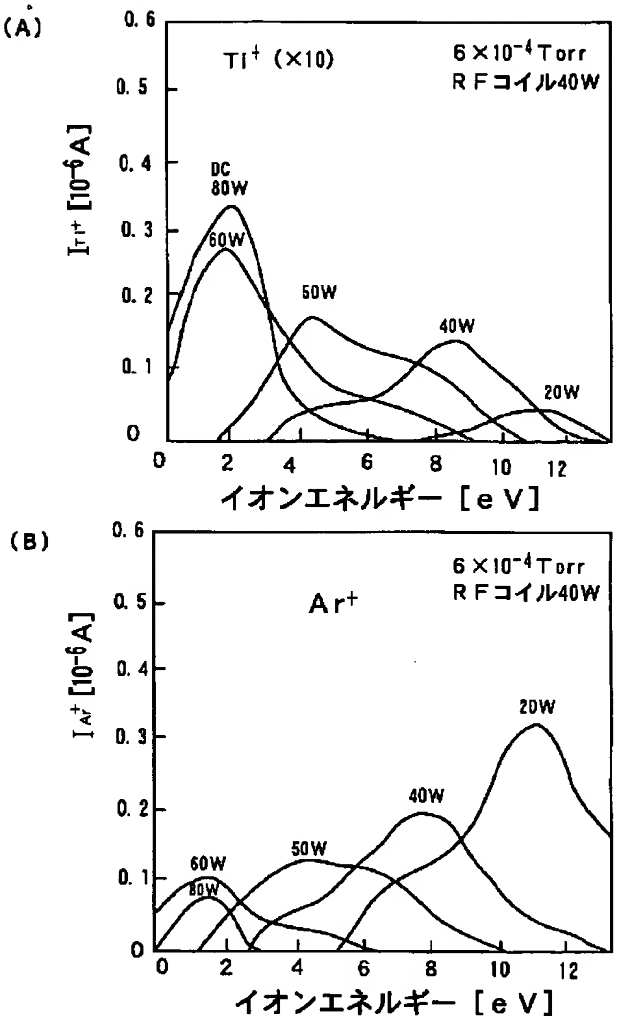
[Drawing 5]



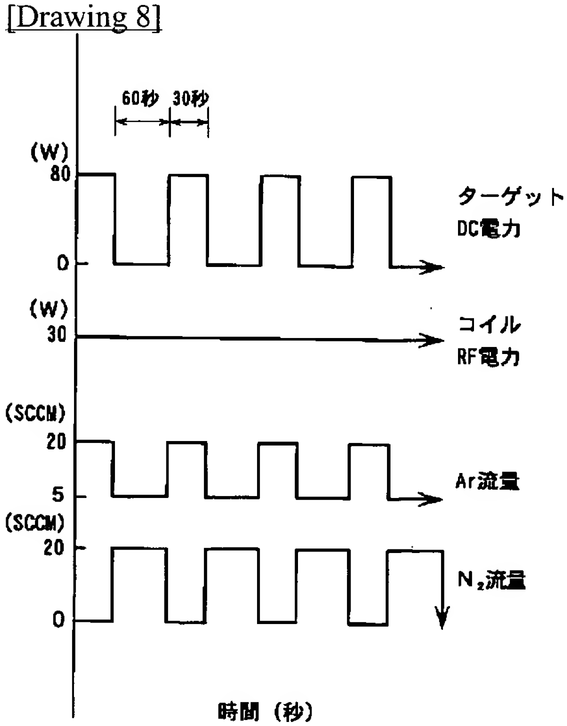
[Drawing 6]



[Drawing 7]


(A)
Ti+ (×10)
6×10-4Torr
RFコイル40W
DC 80W
60W
50W
40W
20W
ITi+ [10-6A]
イオンエネルギー [eV]
(B)
Ar+
6×10-4Torr
RFコイル40W
20W
40W
50W
60W
80W
IAr+ [10-6A]
イオンエネルギー [eV]

[Drawing 8]


60秒 30秒
ターゲット
DC電力
コイル
RF電力
Ar流量
N2流量
時間（秒）

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The cross section showing the membrane formation state of the conventional compound barrier film
[Drawing 2] The distribution map of the composition element of the depth direction of the conventional compound barrier film
[Drawing 3] The cutting side elevation of the equipment used for operation of the method of this invention
[Drawing 4] The property view of voltage impressed to the cathode of drawing 3
[Drawing 5] The related view of RF coil power and the film rate of sedimentation
[Drawing 6] The variation diagram of the film rate of sedimentation when changing target power by making RF coil power into a parameter
[Drawing 7] The correlation diagram of target power, RF coil power, and an ion energy
[Drawing 8] The diagram of the procedure of operation of this invention method
[Drawing 9] The distribution map of the composition element of the depth direction of the film obtained by this invention method
[Description of Notations]
1 Vacuum Chamber, 2 Exhaust Port, 3 Spatter Gas Inlet, 4 Reactant Gas Inlet, 5 DC Power Supply, 6 Metal Target, 7 Magnet, 8 RF Coil, 9 Magnetron Cathode, 10 Unusual Electric Discharge Prevention Circuit, 11 Matching Box, 12 RF Generator, 13 Substrate, 14 Lamp Heater,

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[Translation done.]